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(54) **Powder coating composition containing a resin, a curing agent and zinc.**

(57) The present invention relates to a powder coating composition comprising (a) a resin, (b) a curing agent and (c) zinc, wherein the zinc is a mixture of (c1) lamellar zinc and (c2) zinc dust.

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The invention relates to a powder coating composition comprising (a) a resin, (b) a curing agent and (c) zinc.

Such compositions are generally well-known in the art. See, for example, US4381334 and DE-A-3018765, both of which are incorporated by reference herein for all purposes.

In US4381334, 75-90 % by weight of zinc dust are extruded with a thermosetting binder (an epoxy resin) and, optionally, a curing agent therefor. In DE-A-3018765, 60-90 % by weight zinc dust are extruded with the thermosetting binder and at least an extra 2-25 % by weight zinc dust are then admixed to the ground extrudate. These powder coatings are applied as corrosion protective films.

A disadvantage of these compositions is the appearance of segregation between the resin and zinc dust.

It is, therefore, an object of the invention to provide a powder coating composition containing a resin, for example an epoxy resin, a curing agent and zinc which combines good corrosion protective properties and good film properties.

The invention is characterized in that the zinc is a mixture of (c1) lamellar zinc and (c2) zinc dust.

By using the mixture of zinc dust and lamellar zinc the problem of segregation is very limited because the two zinc components can be totally extruded. The presence of lamellar zinc results in good film properties in combination with good corrosion protective properties.

The present composition also shows good mechanical properties and good adhesion properties. The film properties are compatible to wet zinc containing coatings or coatings obtained by metal sprayed zinc.

According to a preferred embodiment of the invention the powder coating composition contains 10-35 % by weight lamellar zinc and 10-35 % by weight zinc dust. More preferably the composition contains 20-30 % by weight lamellar zinc and 20-30 % by weight zinc dust. % by weight is based upon the combined weight of components (a), (b) and (c).

The powder coating composition according to the invention is preferably based on an epoxy resin. Other suitable resins are in general well-known in the art and include polyesters, polyacrylates, and/or polyurethanes. Mixtures of these resins with epoxy resins, such as epoxy resin-polyester resin mixtures, are also suitable. Such powder coating resins are, again, in general well-known in the art.

According to a further preferred embodiment of the invention the composition comprises:

a + b) 30-70 % by weight epoxy resin and curing agent,

c1) 10-35 % by weight lamellar zinc and

c2) 10-35 % by weight zinc dust.

Zinc dust also includes zinc powder. Zinc dust and zinc powder are particulate forms of zinc. These terms have been used more or less indiscriminately to designate particulate zinc materials. Relatively, zinc dust is smaller in particle size and spherical in shape, whereas zinc powder is coarser in size and irregular in shape.

A suitable zinc dust product can have a particle size between 2 and 500 μm . The apparent density can be for example between 1 and 4 kg/l.

Zinc dust can contain minor amounts, preferably less than 4 % by weight, more preferably less than 1,4 % by weight (based upon the weight of the zinc dust) of other components such as for example lead, cadmium, copper, chloride and/or iron.

Lamellar zinc is characterized by a rather large ratio of the average flake diameter to thickness. A suitable lamellar zinc product can, for example, be characterized as follows:

- volatile content: (DIN 55923)	8 +/- 2 %
- screen analysis: (DIN 53196)	< 45 μm , min. 98 %
- micro sieving:	< 20 μm , min 87 %
- specific gravity:	3,4 kg/l
- average particle size distribution	d ₁₀ 4 μm d ₅₀ 14 μm d ₉₀ 34 μm

Preferably a solvent is added to wet the lamellar zinc. A suitable solvent is for example white spirit. The solvent can be added in amounts between 1 and 15 % by weight, preferably between 6 and 11 % by weight and more preferably between 9 and 10 % by weight (based upon the weight of the lamellar zinc), to the lamellar zinc.

The process for preparing the composition according to the invention includes by preference the following steps: weighing of raw materials, next premixing of raw materials, then an extrusion process,

followed by the grinding process and the storage. The zinc mixture is preferably added at first and included in the premix of raw materials.

Suitable epoxy resins are for example epoxy resins based on epichlorohydrin and 2,2-bis-(4-hydroxyphenyl)-propan with softening points of between 40°C and 90°C and an epoxy equivalent weight of between 450-2000. The softening point is particularly between 50 and 70°C. Other suitable epoxy resins are for example epoxydized phenol-novolac resins with an epoxy weight equivalent of between 160 and 250 and with a softening point of between 40°C and 90°C. The softening point is preferably between 50°C and 70°C. Preferably a diglycidyl ether of bisphenol-A (DGEBA) novolac modified epoxy resin is used.

Suitable curing agents for epoxy resins are for instance, dicyandiamide, imidazole derivatives and imidazoline derivatives, acid anhydrides of trimellitic acid, pyromellitic acid, benzophenonetetracarboxylic acid, tetrahydrophthalic acid, cyclopentanedicarboxylic acid, hexahydrophthalic acid, partly esterified adducts of said carboxylic acids, aromatic amines, phenolic resins (resol or novolac) and epoxy resin-phenol adducts, alone or in combination.

The curing agents can be applied in amounts between 5 and 30 % by weight (based upon the weight of the resin).

The coating composition can also contain, for example, fillers, flow-promoting agents and pigments.

Suitable fillers are generally well-known in the art and include quartz powder, aluminium-, calcium- and magnesium silicates, calcium carbonate, barium sulphate, calcium sulphate and aluminium oxide, mixtures of these, optionally with smaller amounts of e.g. aluminium hydroxide, ammoniumpolyphosphate and the like.

Flow-promoting agents are also well-known in the art and include, by preference, liquid polyacrylates, such as, for instance, polybutylacrylate and polyethylacrylate. Other suitable flow-promoting agents include fluorinated polymers such as, for instance, esters of polyethylene glycol and perfluorooctanoic acid, polymeric siloxanes such as, for instance, polydimethyl siloxane or polymethylphenyl siloxane.

The composition according to the invention can also contain silica containing additives to improve the corrosion protective properties. A suitable compound is "Shieldex" (ex Grace) which can be applied in amounts between for example 2 and 30 % by weight (based upon the total weight of the zinc).

Suitable pigments are, for instance, titanium dioxide, iron oxide (yellow, brown, red, black), carbon black and organic pigments.

If so desired, other well-known additives such as accelerators, release agents and viscosity reducing agents, may also be used.

The obtained powder coatings are especially suitable for application to metals such as iron, steel, copper, aluminium and the like. It is, however, also possible to apply the present coatings to carbon, wood, glass and polymers.

A variety of methods can be used to apply the compositions to various articles and substrates. These methods include flame spraying, (electrostatic) fluidized bed methods, electrostatic spraying, plasma spraying and tribocharging methods.

Electrostatic powder or tribo spraying methods charge the particles with the aid of a powder gun the particles and spray them towards a grounded steel substrate. Because the powder is not conductive the particles stick on the metal due to electrostatic attraction forces. The object can then be placed in an oven for curing of the powder coating.

The fluidized bed method is quite simple and can best be described as a "hot dip process". A preheated object is dipped in a fluidized bed of powder. The powder sticks and melts on the metal surface. After dipping the object is put in an oven for curing.

Preferably the coating composition according to the invention is applied to a sand blasted or chemically treated substrate in a layer thickness which is preferably between 40 and 60 µm. Before or after curing of this layer a second layer is applied as a topcoat coating in a layer thickness which is preferably between 60 and 80 µm. The second layer is preferably a powder coating composition based on a polyester resin as binder and an epoxy group containing component, such as triglycidylisocyanurate, as curing agent.

In general after applying uncured powder coating on steel or other materials, the powder coating is cured. Curing temperatures and times can vary from for example 160°C to 220°C and 1 minute to 15 minutes. On curing the powder particles will start to melt and fuse together. As the temperature rises so the viscosity drops, giving the coating flowing opportunity. The process continues until the curing agent starts crosslinking with the resin, and then the viscosity will rapidly increase. It is important that for good glow and minimal "orange peel" that a rapid heat up occurs. The cure time and temperature have considerable influence on the mechanical properties.

The invention will be further illustrated by the following examples:

ExamplesExample I5 Preparation of the powder coating composition

25 parts by weight zinc dust (standard zinc powder, ex Vieille-Montagne), 25 parts by weight lamellar zinc (Ecka-4 ex Eckart) and 50 parts by weight of a DGEBA novolac modified epoxy resin with phenolic hardener (weight ratio resin: hardener 7:3) were mixed at a temperature of 100°C in an extruder. After
10 addition of 0.1% by weight pyrogenic silica, the grinding process followed.

Example IIProtection of the outside of a gas tank

15 First the steel of the tank was sandblasted. Next the tank was preheated to 240°C. After that the powder coating composition obtained according to Example I was electrostatic applied in a layer thickness of 50 µm. Next the second layer consisting of a composition containing a polyester resin and TGIC crosslinker in a weight ratio 93:7 was applied in a layer thickness of 70 µm. The curing took place at a
20 temperature of 180°C during 10 minutes.

The corrosion resistance was determined by the ability of the coating to retain adhesion while subjected to corrosive salt spray (SIO 1456, ASTM B 117). After 1000 hours of exposure no loss of adhesion was reported. Also no blistering had been reported.

The Erichsen slow penetration test (ISO 1520; determination of the flexibility) resulted in 4 mm.

25 The determination of the adhesion properties (ISO 2409) resulted in GT-0 which means that there was no loss of adhesion.

The impact resistance (ISO 6272) was 0,5 kg/m.

It could be concluded that a powder coating composition to the invention resulted in a combination of good corrosion protective properties and good film properties.

Claims

1. A powder coating composition comprising (a) a resin, (b) a curing agent and (c) zinc, characterized in that the zinc is a mixture of (c1) lamellar zinc and (c2) zinc dust.
- 35 2. The powder coating composition according to claim 1, characterized in that the powder coating comprises 10-35 % by weight lamellar zinc and 10-35 % by weight zinc dust, % by weight being based upon the total weight of (a), (b) and (c).
- 40 3. The powder coating composition according to claim 2, characterized in that it comprises:
(a + b) 30-70 % by weight of the resin and curing agent,
(c1) 10-35 % by weight lamellar zinc and
(c2) 10-35 % by weight zinc dust,
% by weight being based upon the total weight of (a), (b) and (c).
- 45 4. The powder coating composition according to any one of claims 1-3, characterized in that the resin comprises an epoxy resin.
5. The powder coating composition according to claim 4, characterized in that the epoxy resin comprises
50 an epoxydized phenol-novolac resin.
6. The powder coating composition according to any one of claims 1-5, characterized in that the lamellar zinc is wetted with a solvent.
- 55 7. A method of coating a substrate by applying a layer of the powder coating according to any one of claims 1-6 onto a substrate, applying a topcoat onto the layer of the powder coating and curing.
8. The method according to claim 7, characterized in that the topcoat is a powder coating.

9. The method according to any one of claims 7-8, characterized in that the substrate is a steel gas tank.
10. The use of a mixture of zinc dust and lamellar zinc in order to improve the combination of film properties and corrosion protective properties of a zinc-containing powder coating composition.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2200

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	DE-A-3 704 479 (METALON STOLBERG) * column 3, paragraph 2; claims 1,4,5 * ---	1,2,6	C09D5/03 C09D5/10 C09D163/00
A,D	US-A-4 381 334 (LEIZER BALK) * claim 1 * -----	1,4	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 OCTOBER 1992	Examiner GIRARD Y.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- @ : member of the same patent family, corresponding document	

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